



An analytical study of a lead-acid flow battery as an energy storage system



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HIGHLIGHTS

- 2D lead-acid flow battery simulation which gives valuable mechanisms including electrochemical and surface reactions.
- Simulations successfully show surface concentrations of PbO and PbO₂ on the positive electrode.
- Simulations have shown that velocity is an important aspect when investigating lead deposition onto the electrodes.
- Effects of cell temperature, applied current density, initial species concentration, and external voltage were studied.

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ABSTRACT

The most important issue with our current clean energy technology is the dependence on environmental conditions to produce power. To solve this problem a wide range of energy storage devices are being explored for grid-scale energy storage including soluble lead-acid flow batteries. Flow batteries offer a unique solution to grid-scale energy storage because of their electrolyte tanks which allow easy scaling of storage capacity. This study seeks to further understand the mechanisms of a soluble lead acid flow battery using simulations. The effects of varies changes to operating conditions and the system configuration can be explored through simulations. The simulations performed are 2D and include the positive electrode, negative electrode, and the flow space between them. Simulations presented in this study show Pb(II) surface concentration, external electric potential, and PbO/PbO₂ surface concentration on the positive electrode. Simulations have shown increasing cell temperature can increase external electric potential by as much as 0.2 V during charge. Simulations have also shown electrolyte velocity is an important aspect when investigating lead deposition onto the electrodes. Experimental work was performed to validate simulation results of current density and voltage. Good correlation was found between experimental work and simulation results.

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1. Introduction

Why do we need energy storage? Political instability in oil-rich countries makes it risky for the U.S. to continue its reliance on petroleum. Furthermore, the use of fossil fuels for heat and power contributes to environmental pollution and global warming. There is no single solution to the pending energy crisis. A combination of solutions (solar, wind, biomass, hydrogen, and/or fuel cells) will be required to meet our future energy needs. This is because the

output of renewable sources varies by environmental conditions. For example, the range of output from solar power and wind power generation depends on the weather. Grid-scale energy storage that is efficient and competitive in pricing remains a missing piece of the renewable energy puzzle.

Lead-acid flow batteries are a promising technology for grid-scale energy storage. Flow batteries can be easily scaled to fit any system requirements making them optimal for load leveling. When energy storage must be increased, all that needs to be changed is the capacity of the electrolyte storage tanks. Lead-acid flow batteries offer a high energy density and cell voltage when compared to vanadium or zinc flow batteries. The cost of producing a lead-acid battery is much lower than most flow batteries as the electrolyte is easily obtained and no proton exchange membrane is required.

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Nomenclature

c_i	species concentration [mol m^{-3}]	p_{entr}	laminar entrance pressure [Pa]
c_{O_i}	initial concentration [mol m^{-3}]	ϕ_{il}	electrolyte potential [V]
c_{S_i}	surface concentration [mol m^{-3}]	ϕ_{isext}	external electric potential [V]
D_i	diffusivity coefficient [$\text{m}^2 \text{s}^{-1}$]	Q_i	heat flux [W m^{-2}]
E_{eq}	equilibrium potential [V]	Q_s	power dissipation [W]
$E_{0,\text{eq}}$	ambient equilibrium potential [V]	R	universal gas constant [$\text{J (mol}^{-1} \text{K}^{-1})$]
E_{pos}	equilibrium potential at positive electrode [V]	$R_{i,\text{src}}$	reaction rate
F	Faraday's constant [C mol^{-1}]	$R_{i,\text{tot}}$	total rate expression
i_{app}	applied current density [A m^{-2}]	$R_{i,\text{m}}$	local rate expression
i_{cycle}	current density per cycle [A m^{-2}]	$R_{s,i}$	surface rate expression
i_{dl}	current density at the electrode surface [A m^{-2}]	T	fluid temperature [K]
i_l	local current density [A m^{-2}]	T_{ref}	reference temperature [K]
i_s	source current density [A m^{-2}]	tflux_i	total flux in y -direction [$\text{mol (m}^{-2} \text{s}^{-1})$]
$i_{\text{loc,m}}$	local current density per unit mass [$\text{A (m}^{-2} \text{kg}^{-1})$]	u_i	boundary flow velocity [m s^{-1}]
i_{total}	total current density [A m^{-2}]	$\mathbf{u}_{\text{m},i}$	flow velocity [m s^{-1}]
i_0	open circuit current density [A m^{-2}]	Z_i	valance/charge number
k_{Ob_i}	backward rate constant [$\text{m}^4 (\text{s}^{-1} \text{mol}^{-1})$]	α_a	anode stoichiometric coefficient
k_{Of_i}	forward reaction rate constant [$\text{m}^4 (\text{s}^{-1} \text{mol}^{-1})$]	α_c	cathode stoichiometric coefficient
k_{O_i}	rate constant [m s^{-1}]	ρ	density [kg m^{-3}]
l	length of the section [m]	ϕ_s	electrode electric potential [V]
L_{entr}	laminar flow entrance length [m]	ϕ_l	electrolyte electric potential [V]
$\mathbf{n}$	normal vector	$\sigma_{i,s}$	site occupancy number
$\mathbf{N}_i$	concentration flux [$\text{mol (m}^{-3} \text{s}^{-1})$]	μ	dynamic viscosity [Pa s]
n_m	number of participating electrons	$\nu_{i,m}$	stoichiometric coefficient
p_i	pressure [Pa]	θ_i	fraction of free sites
		Γ_s	density of sites [mol m^{-2}]

The biggest challenge in lead-acid flow battery technology is lead deposition on the electrodes. Overtime the process of deposition and removal degrades the electrode efficiency reducing the performance of the flow battery. Life cycle is very important to grid-scale energy storage. Reduction in efficiency and replacing electrodes costs money in materials, training, and service. Several solutions to the problem of lead deposition have been explored; however, none offer a solution that allows for an extended life time. Very few analytical studies have been done on the soluble lead-acid flow battery. Experimental work was performed to validate simulation results.

Gu, Nguyen, and White developed a mathematical model of a lead acid cell [1]. They based their mathematical model on the assumption that the cell geometry and structure can be considered as one uniform macroscopic unit with charge transfer and other transport effects taking place normal to the longitudinal direction [1]. Gu et al. showed that the exchange current density is dependent on the working temperature [1]. Also, the cell geometry affects the output; a thin positive electrode influences the output voltage more than a thick one. The authors attributed this to a greater degree of polarization in the thin positive electrode. Porosity also has a strong influence on the cell as electrodes having greater porosity have greater discharge times [1].

Mauracher and Karden used impedance spectroscopy to study the dynamic model of lead acid batteries [2]. Their study was based on the principle that phenomenological models requiring several parameters seldom sufficiently predict the different conditions of the cell. Instead they based their model on the physicochemical elements of the cell. The differential equations for the working of the cell were developed considering a stationary electrolyte and then solved and the solutions were considered equivalent to an electric circuit. The model was developed based on Randles equivalent circuit and then an equilibrium voltage was obtained in the case of no current. The authors were able to find out the

concentration overvoltage values based on the state of charge and input current [2].

Simulation along with experimental verification of the lead acid battery system was done by Achaibou et al. [3]. They developed their model considering that active parts of both anode and cathode convert to lead sulfate during discharge and charging results in liberation of sulfate ions and thereby causes an increase in electrolyte concentration. Based on the voltages obtained and the currents applied the authors showed that voltages varied linearly with time for different applied currents at 25 °C. The authors were able to correlate similar results from the experimental study of a lead acid battery. Root mean square error values showed that the model fits closely with experimental results. Errors in the model were attributed to the specificity of the experimental conditions with respect to the model which was deemed to be more generic [3].

Shah et al. developed a transient, analytical model for an all vanadium flow battery and compared it to experimental results [4]. The analytical model considers mass transport, charge transport, electrode surface reactions, and electrochemical effects [4]. It is a 2D model with a domain that includes two electrodes, two reservoirs, and an electrolyte membrane. Mass balance controls charged species concentrations in the electrolyte and on the electrode surface. Charged species transport includes diffusion, migration, and convection. The electrolyte is treated as incompressible and as a dilute-solution with water being the dominant component [4]. The thickness of deposited layers on the electrodes is assumed small compared to the inner electrode gap. This is a good approximation at low cycle numbers; however, the thickness of the electrodeposited layers has an increased effect as cycle numbers increase [4]. The system is assumed isothermal. Shah et al. report the simulation results have a good degree of accuracy in reporting trends based on experimental data [4].

Shah et al. developed a transient model for a lead-acid flow battery incorporating mass transport, charge transport, and

surface electrode reactions [5]. Equations used by Shah et al. closely match the equations used in this study including the Nernst-Plank and Butler–Volmer equations. Analytical results were compared to experimental data. The experimental cell used 10×10 cm electrodes and had an interelectrode gap of 1.2 cm [5]. The electrolyte had a volume of 1500 cm^3 and was composed of methane sulfonate, methanesulfonic acid, and hexadecyltrimethylammonium hydroxide [5]. The electrolyte flow rate was $2.3\text{--}6.9 \text{ cm s}^{-1}$ at a current density of 10 mA cm^{-2} [5]. Analytical parameters used by Shah et al. closely match those used in this study. A good correlation was found between analytical and experimental work [5].

Oury et al. studied a lead acid battery from a mathematical standpoint [6]. The authors assumed that the source of the active species to the cell remains constant and therefore the amount of electrolyte is infinite [6]. COMSOL multiphysics was used for studying the model. Results showed that the reaction kinetics improve at increased current levels at the electrode edges [6]. Also, the discharge voltage demonstrates a progressive increase with greater number of cycles [6].

The goal of this study is to explore simulations that allow for the adjustment of operating conditions and observation over charge/discharge cycles. Variations in cell temperature, applied current density, inlet electrolyte velocity, and initial species concentrations were investigated. Simulations performed for this study were of a charge, discharge, and charge cycle. Results presented include electrode surface concentrations for anode and cathode, external electric potential versus time, and positive electrode surface concentration versus time.

Experimental work was performed to validate current density and voltage results of simulation. The experimental set up involved a cell in which the electrolyte was lead methanesulfonate in methanesulfonic acid at a concentration of 500 mol m^{-3} to be consistent with simulation. A three electrode setup was used for the process. The counter electrode was platinum coated fluorinated tin oxide (FTO) glass, the working electrode was graphite, and the reference electrode was silver/silver chloride. The active area of the working electrodes were 4 cm^2 and a current density of 15 mA cm^{-2} was applied in three different cycles to match simulation. The first cycle charged for 1 h, the second cycle discharged for 1 h, and the last cycle charged for 1 h. All measurements were done under room temperature conditions.

2. Simulation setup

Simulations are of a single cell lead-acid flow battery during a charge, discharge, and charge cycle. The simulations are 2D and include both anode and cathode electrodes and the fluid region between them. The electrodes are 10 cm long with an active area of 100 cm^2 and the electrode depth out of the plane is 10 cm. The negative and positive electrodes are separated by a 12 mm gap where the electrolyte flows. Input parameters are shown in Table 1. If not specified, the initial values of a simulation are those shown in Table 1. Input parameters and equations are very similar to those used by Shah et al. in their analytical study which was experimentally validated [5].

Several assumptions were applied during development of the simulations. Flow is considered 2D and isotropic in order to simplify the model and reduce simulation time. Laminar flow is assumed because the electrolyte flow rate is relatively low. The electrolyte mixture only dissociates into Pb^{2+} , H^+ , and HSO_4^- and good tank mixing is assumed. The negative electrode is modeled as grounded and electric potential in the electrodes is assumed to be space independent. Induced convection due to electrochemical reactions at the electrode surface is assumed negligible allowing for

Table 1
Parameter values and initial values for simulations.

Name	Value	Description
c_{OH}	500 mol m^{-3}	Initial hydrogen ion concentration in the electrolyte.
$c_{\text{OPb(II)}}$	500 mol m^{-3}	Initial Pb(II) concentration in the electrolyte.
D_{H}	$9.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$	Diffusion coefficient of hydrogen ion in the electrolyte.
D_{HSO_4}	$1.33 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$	Diffusion coefficient of HSO_4^- ion in the electrolyte.
$D_{\text{Pb(II)}}$	$0.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$	Diffusion coefficient of Pb(II) in the electrolyte.
i_{app}	200 A m^{-2}	Applied current density.
k_{Ob}	$4.5 \times 10^{-7} \text{ m}^4 (\text{mol}^{-1} \text{ s}^{-1})$	Backward rate constant for PbO reaction.
k_{Of}	$k_{\text{Ob}} * 10000 \text{ m}^4 (\text{mol}^{-1} \text{ s}^{-1})$	Forward rate constant for PbO reaction.
k_{Opb}	$2.1 \times 10^{-7} \text{ m s}^{-1}$	Rate constant for the negative electrode reaction.
$k_{\text{OPb(II)}}$	$2.5 \times 10^{-7} \text{ m s}^{-1}$	Rate constant for the positive electrode reaction.
p_{out}	300 kPa	Outlet pressure.
T	300 K	Initial temperature.
u_{in}	0.023 m s^{-1}	Inlet boundary flow velocity.
z_{H}	1	Charge number.
z_{HSO_4}	−1	Charge number.
$z_{\text{Pb(II)}}$	2	Charge number.
Γ_s	$2 \times 10^{-5} \text{ mol m}^{-2}$	Density of sites.

the solution of flow conditions as a stationary model. Fig. 1 displays a flow chart of the modeling concept used for simulation.

2.1. Laminar flow

The laminar flow module solves for the velocity field and pressure of the electrolyte. Flow is considered compressible and the dependent variables, pressure and velocity, are calculated with

$$\rho(\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot \left[-p \mathbf{I} + \mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} \mu (\nabla \cdot \mathbf{u}) \mathbf{I} \right] + F \quad (1)$$

and

$$\nabla \cdot (\rho \mathbf{u}) = 0. \quad (2)$$

The flowing electrolyte is primarily water, so water properties are used for density and viscosity. The inlet flow boundary is considered laminar inflow and the inlet velocity field is calculated with

$$L_{\text{entr}} \nabla_t \left[-p_{\text{entr}} \mathbf{I} + \mu (\nabla_t \mathbf{u} + (\nabla_t \mathbf{u})^T) \right] = -p_{\text{entr}} \mathbf{n} \quad (3)$$

where L_{entr} is 0.01 m. The outlet velocity field is calculated at an outlet pressure of 300 kPa with

$$\left[\mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} \mu (\nabla \cdot \mathbf{u}) \mathbf{I} \right] \cdot \mathbf{n} = 0. \quad (4)$$

The values obtained from the equations above, solved for as a stationary system, are used for electrolyte flow values in the time dependent study.

2.2. Time dependent – charge/discharge

The following subsections were employed to simulate the model as a time dependent study. The simulation starts with charging for 60 min (3600 s) followed by a 60 s rest time. Then discharge is

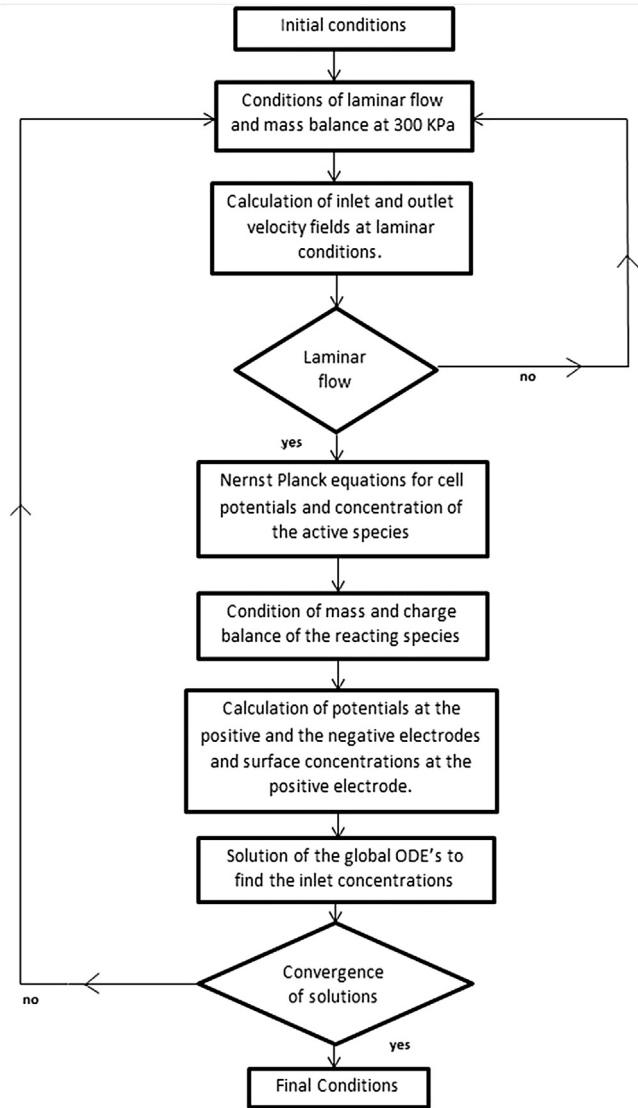


Fig. 1. Flow chart of the modeling concept followed for simulations.

simulated for 60 min followed by another rest period and finally, 60 min of charging.

2.2.1. Tertiary current distribution, Nernst–Planck

Nernst–Planck equations are used to solve for the electric potential of the cell and concentration of active species in the electrolyte. The dependent variables, species concentrations (Pb(II), H^+ , and HSO_4), electrolyte potential, and electric potential, are calculated using

$$\nabla \cdot (-D_i \nabla c_i - z_i \mathbf{u}_{m,i} F c_i \nabla \phi) + \mathbf{u} \cdot \nabla c_i = R_{i,src}, \quad (5)$$

$$\nabla \cdot \mathbf{i}_l = F \sum_i z_i R_{i,src} Q_i, \quad (6)$$

$$\sum_i z_i c_i = 0, \quad (7)$$

$$\mathbf{N}_i = -D_i \nabla c_i - z_i \mathbf{u}_{m,i} F c_i \nabla \phi + \mathbf{u} c_i, \quad (8)$$

$$\mathbf{i}_l = F \sum_i z_i (-D_i \nabla c_i - z_i \mathbf{u}_{m,i} F c_i \nabla \phi), \quad (9)$$

$$\nabla \cdot \mathbf{i}_s = Q_s, \quad (10)$$

and

$$\mathbf{i}_s = -\sigma_s \nabla \phi_s. \quad (11)$$

The initial concentration of HSO_4 is derived from electro-neutrality. The diffusion coefficient for Pb(II) is $0.7 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, H^+ is $9.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, and HSO_4 is $1.33 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. Migration in the electric field is calculated using Eq. (8). The charge number for Pb(II) is 2, H is 1, and HSO_4 is -1.

Electric potential is set to zero and electrolyte potential, ϕ_{il} , is solved with

$$\phi_{il} = \frac{RT}{2F} \log \left(\frac{c_{Pb(II)}}{1000} \right). \quad (12)$$

Governing equations for the electrolyte–electrode boundary interface that solve for local current densities and rate expressions are:

$$\mathbf{i}_l \cdot \mathbf{n} = i_{total} \quad (13)$$

$$i_{total} = \sum_m i_m + i_{dl} \quad (14)$$

$$-\mathbf{n} \cdot \mathbf{N}_i = R_{i,tot} \quad (15)$$

$$R_{i,tot} = \sum_j R_{i,m} \quad (16)$$

The negative electrode reaction potential is calculated with

$$\eta = \phi_{s,ext} - \phi_l - E_{eq}. \quad (17)$$

Equilibrium potential at the negative positive electrode is calculated with

$$E_{eq} = E_{0,eq} + \frac{dE_{eq}}{dT} (T - T_{ref}). \quad (18)$$

Electrode kinetics are calculated using the Butler–Volmer equation

$$i_{loc} = i_0 \left(\exp \left(\frac{\alpha_a F \eta}{RT} \right) - \exp \left(\frac{-\alpha_c F \eta}{RT} \right) \right) \quad (19)$$

where

$$i_0 = F^* k_{ObPb}^* c_{Pb(II)}. \quad (20)$$

The anodic and cathodic transfer coefficients are 1. The local rate expression is calculated using

$$R_{i,m} = \frac{\nu_{i,m} i_{loc,m}}{n_m F} \quad (21)$$

where the number of participating electrons is 2 and the stoichiometric coefficients are -1 for Pb(II) and 0 for H and HSO_4 .

The positive electrode is evaluated using equations (13)–(16) plus one additional equation,

$$\int_{\partial\Omega} (\mathbf{n} \cdot \mathbf{i}_l) d\mathbf{l} = i_{l,avg} \int_{\partial\Omega} d\mathbf{l} \quad (22)$$

to solve for current density by integrating over the electrode boundary.

To get the average current density over the full cycle, the equation

$$i_{l,avg} = i_{cycle} = i_{app}(\text{charge1}(t) - \text{discharge1}(t) + \text{charge2}(t)) \quad (23)$$

is used where i_{app} is manually varied, the charge time is 60 min, discharge time is 60 min, and the rest period between each is 60 s. Boundary electric potential for the positive electrode is calculated using

$$\phi_{s,ext} = 1.8 - \frac{RT \log\left(\frac{c_{Pb(II)}}{1000}\right)}{2F} - 4 \log\left(\frac{c_H}{1000}\right) - \frac{RT}{2F} \log\left(\frac{c_{Pb(II)}}{1000}\right). \quad (24)$$

The positive electrode has two electrode reaction nodes both using Eq. (17) for electrode reaction and Eq. (18) for equilibrium potential. To solve electrode kinetics in the first electrode reaction node

$$i_0 = F * k_{O_{PbO_2}} * c_{Pb(II)} * \frac{c_H}{c_{O_H}} \quad (25)$$

is used, a slightly modified version of Eq. (20). The anodic and cathodic transfer coefficients are both 0.5. Eq. (19) is used to find local current density for electrode reaction 1. The number of participating electrons is 2 and the stoichiometric coefficient for Pb(II) is 1, H is -4, and HSO₄ is 0. The second electrode reaction of the positive electrode uses

$$i_{loc} = F \left(k_{Of} * (c_{PbO})^2 * \exp\left(\frac{F(\phi_{isext} - \phi_{il} - E_{pos})}{RT}\right) - c_H * c_{PbO_2} * k_{Ob} * \exp\left(\frac{-F(\phi_{isext} - \phi_{il} - E_{pos})}{RT}\right) \right) \quad (26)$$

to solve for local current density. The number of participating electrons is 2 and the stoichiometric coefficient for Pb(II) is 0, H is -2, and HSO₄ is 0.

2.2.2. Surface reactions

At the positive electrode PbO is electrodeposited during discharge and stripped during charge. Also at the positive electrode, PbO₂ is being electrodeposited during charge and stripped during discharge. This action calls for surface reaction boundary

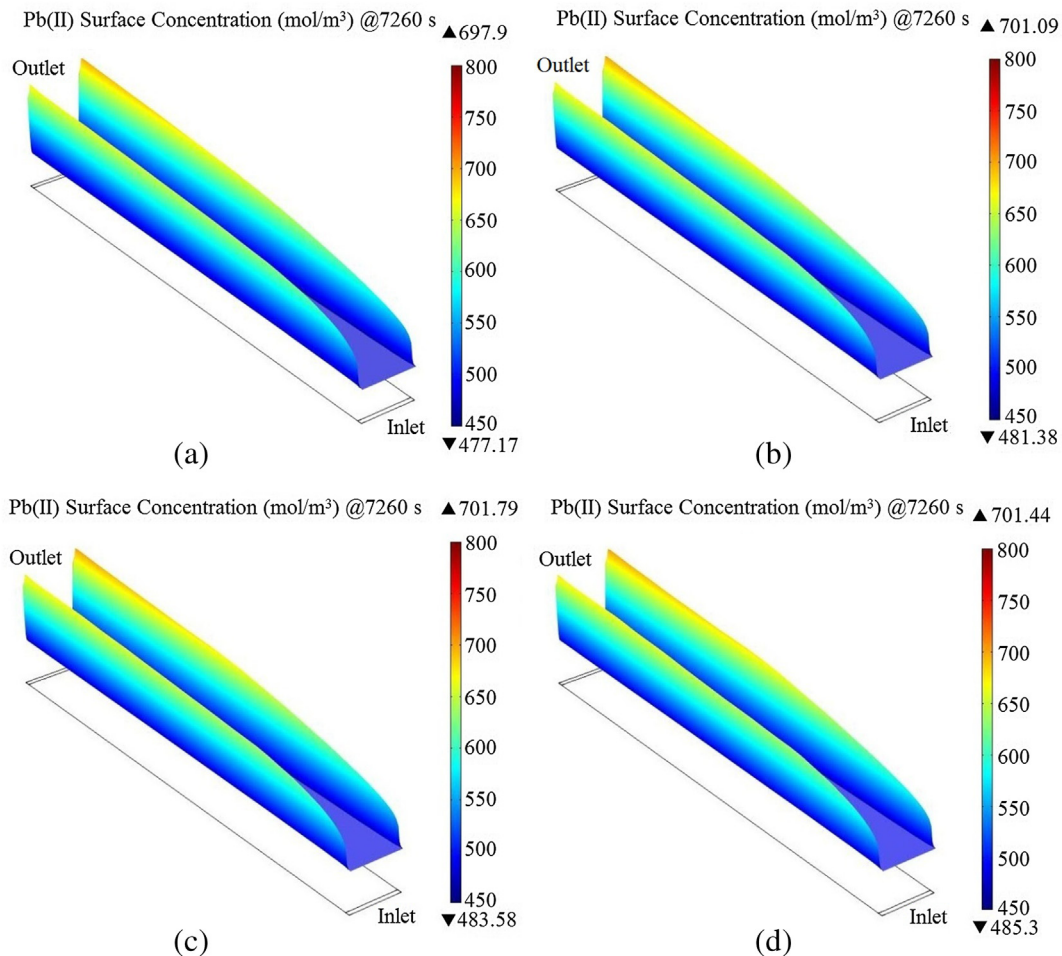


Fig. 2. Pb(II) surface concentration on the positive and negative electrode. (a) $T = 300$ K (b) $T = 350$ K (c) $T = 400$ K (d) $T = 600$ K.

equations to properly account for the concentration of species on the electrode surface. The boundary equations solve for the surface concentrations of PbO and PbO₂ on the positive electrode surface. The governing equations for calculating surface concentrations are

$$\nabla_t(-D_i \nabla_t c_{s,i}) = R_{s,i}, \quad (27)$$

$$N_i = -D_i \nabla_t c_{s,i}, \quad (28)$$

$$\theta_i = \frac{c_{s,i} \sigma_i}{F_s}, \quad (29)$$

and

$$\frac{\partial c_{b,i}}{\partial t} = R_{b,i}. \quad (30)$$

Site density is $2 \times 10^{-5} \text{ mol m}^{-2}$, site occupancy number for Pb and PbO₂ is 1. Reaction effects are taken into account by using two electrode–electrolyte interface couplings. For the first coupling, local current density is taken from the first electrode reaction of the positive electrode. Eq. (21) is used with 2 participating electrons. The stoichiometric coefficients are 0 for PbO and -1 for PbO₂. The second coupling uses local current density from the second electrode reaction of the positive electrode. Coefficients are the same.

2.2.3. Global ODEs and DAEs

The global ODEs and DAEs module is used to control the concentration values for lead ions and protons in the electrolyte. Lead ion inlet concentration is calculated using

$$F(u, u_t, u_{tt}, t) = c_{\text{Pb(II)}} - \frac{L}{V} \left(\int_{\text{outlet}} (tfluxy_{c_{\text{Pb(II)}}}) - \int_{\text{inlet}} (tfluxy_{c_{\text{Pb(II)}}}) \right) = 0, \quad (31)$$

$$u(t_0) = u_0 = c_{\text{O}_{\text{Pb(II)}}}, \quad (32)$$

and

$$u_t(t_0) = u_{t0} = 0. \quad (33)$$

Proton inlet concentration is calculated using equations (31)–(33) however $c_{\text{Pb(II)}}$ is replaced with c_{H} , $c_{\text{O}_{\text{Pb(II)}}}$ is replaced with $c_{\text{O}_{\text{H}}}$, and the total flux values are of H. HSO₄ is accounted for by electroneutrality.

3. Results and discussion

Surface concentrations near the anode and cathode electrodes are shown in Figs. 2–5. The left boundary is the anode electrode

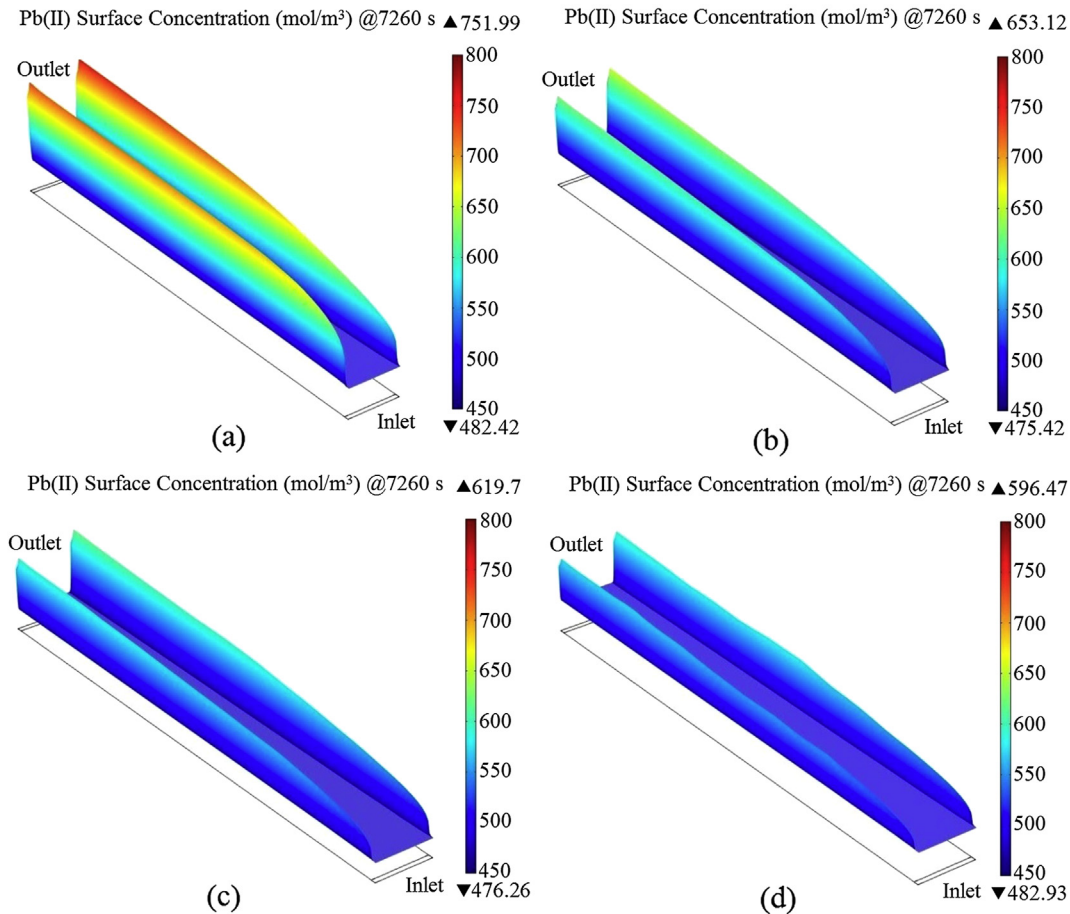


Fig. 3. Pb(II) surface concentration on the positive and negative electrode. (a) $U_{in} = 0.01 \text{ m s}^{-1}$ (b) $U_{in} = 0.05 \text{ m s}^{-1}$ (c) $U_{in} = 0.1 \text{ m s}^{-1}$ (d) $U_{in} = 0.2 \text{ m s}^{-1}$.

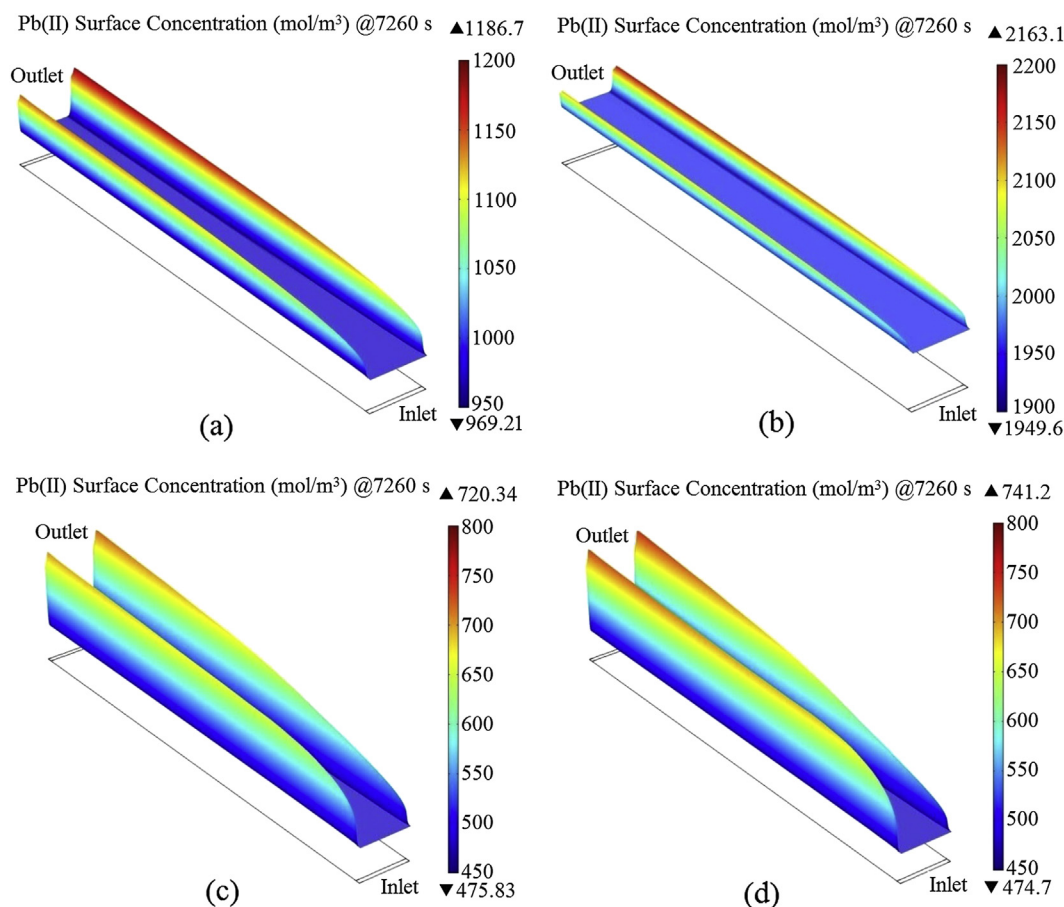


Fig. 4. Pb(II) surface concentration on the positive and negative electrode. (a) $c_{\text{Pb(II)}}^{\text{initial}} = 1000 \text{ mol m}^{-3}$ (b) $c_{\text{Pb(II)}}^{\text{initial}} = 2000 \text{ mol m}^{-3}$ (c) $c_{\text{H}}^{\text{initial}} = 1000 \text{ mol m}^{-3}$ (d) $c_{\text{H}}^{\text{initial}} = 2000 \text{ mol m}^{-3}$.

and the right boundary is the cathode electrode. The images show the concentration of Pb(II) in the electrolyte, close to the electrodes, stretched up so the concentration gradient can be clearly seen. Fig. 2(a–d) shows surface concentrations for Pb(II) at the end of the discharge phase of the cycle. Fig. 2 shows a very small decrease in Pb(II) surface concentrations at increased temperature. Pb(II) surface concentration is in the range of 697–702 mol m^{-3} for all temperatures simulated. Increasing the operating temperature does not appear to have a significant effect on surface concentration.

Surface concentrations of Pb(II) at various electrolyte inlet velocities, at the end of the discharge phase, are shown in Fig. 3(a–d). It is seen from Fig. 2 that electrolyte inlet velocity has a large effect on the surface concentration of Pb(II) and by extension the rate of lead deposition. It cannot be said from the figures this is a solution; however, electrolyte inlet velocity should be considered when investigating ways to control lead deposition in a lead-acid flow battery. At 0.01 m s^{-1} , Fig. 3(a), the surface concentration reaches 752 mol m^{-3} . When the electrolyte inlet velocity is increased to 0.2 m s^{-1} , Fig. 3(d), decreases to a maximum of 597 mol m^{-3} near the outlet of the cell. Increasing the flow velocity 20 times decreased maximum Pb(II) surface concentration by 150 mol m^{-3} , a 21% decrease.

Fig. 4(a–d) shows Pb(II) surface concentrations at the end of the discharge phase resulting from different initial values of Pb(II) and hydrogen. Initial concentrations for both species were set to 500 mol m^{-3} . As expected, increasing initial Pb(II) concentration in the electrolyte, Fig. 4(a, b), increases the surface concentration of

Pb(II) by almost the same amount. In Fig. 4(a) initial Pb(II) concentration is set to 1000 mol m^{-3} , twice the original amount, and this increased Pb(II) surface concentration from around 700 mol m^{-3} to over 1100 mol m^{-3} . Fig. 4(c, d) show Pb(II) surface concentrations resulting from an increase in the initial hydrogen concentration in the electrolyte. The result is a slight increase in the surface concentration of Pb(II). Doubling the initial hydrogen concentration increased the maximum Pb(II) surface concentration by 20 mol m^{-3} .

The effects of changing the applied current density on Pb(II) surface concentrations are shown in Fig. 5(a–c). Fig. 5 shows the applied current density has a fairly significant effect on Pb(II) surface concentrations. Decreasing current density decreases Pb(II) concentration, shown in Fig. 5(a). Increasing current density to 25 mA cm^{-2} , shown in Fig. 5(c), increases Pb(II) concentration by roughly 30 mol m^{-3} over the 10 mA cm^{-2} case. It appears Pb(II) surface concentration is affected more heavily by higher current densities.

Figs. 6–8 and 13 displays the external electric potential versus time of the cell for various changes in operating conditions. Figs. 6–13 includes a charge, discharge, and charge phase. The charge and discharge phases last for 60 min with a 60 s rest period between them. Fig. 6 shows external voltage versus time for changes in inlet velocity. It is seen from Fig. 6 that reducing inlet velocity of the electrolyte slightly increases external voltage during charge and very slightly lowers voltage during discharge. Changes in external cell voltage based on inlet velocity are in the range of only 0.1 V. Fig. 7 shows changes in external electric potential versus time

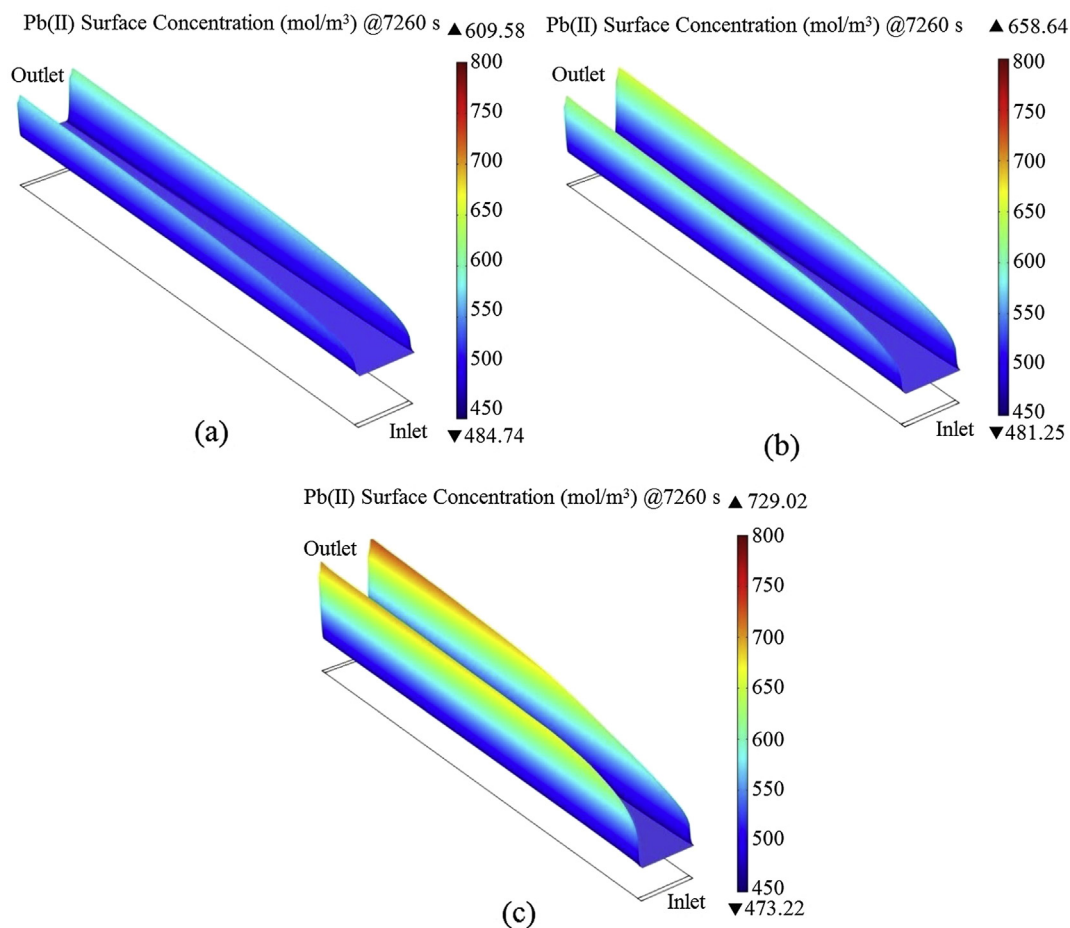


Fig. 5. Pb(II) surface concentration on the positive and negative electrode. (a) $i_{app} = 10 \text{ mA cm}^{-2}$ (b) $i_{app} = 15 \text{ mA cm}^{-2}$ (c) $i_{app} = 25 \text{ mA cm}^{-2}$.

resulting from changes in initial electrolyte concentrations. From Fig. 7 it is seen that increasing the initial concentration of Pb(II) in the electrolyte reduces the external voltage during charge, external voltage is only slightly affected during discharge. Fig. 7 also shows increasing initial hydrogen concentration in the electrolyte slightly

increases the external cell voltage during charge and discharge, more notably during discharge where cell voltage is around 1.69 V. Fig. 7 shows the second charge section, from 7200 s on, does not achieve its original external voltage until half the charge duration has passed. This is a result of surface concentrations from the first

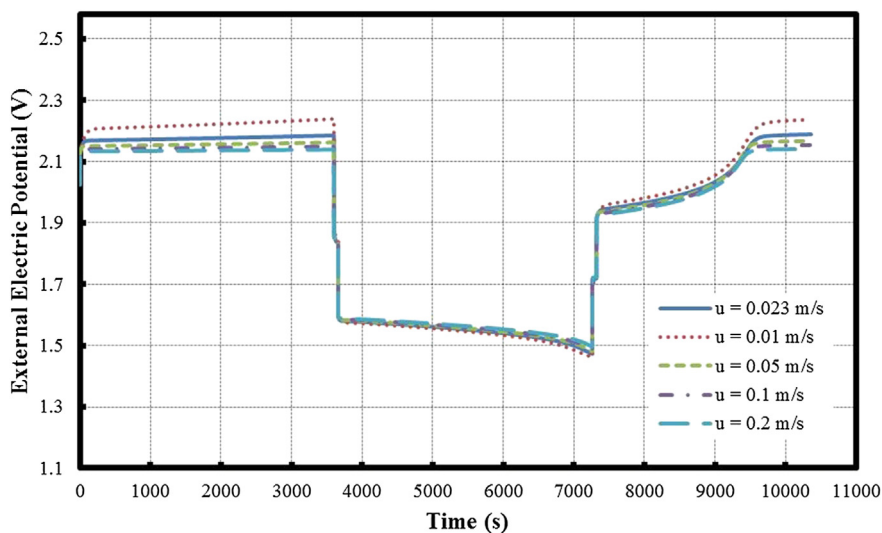


Fig. 6. External electric potential versus time for changes in inlet velocity.

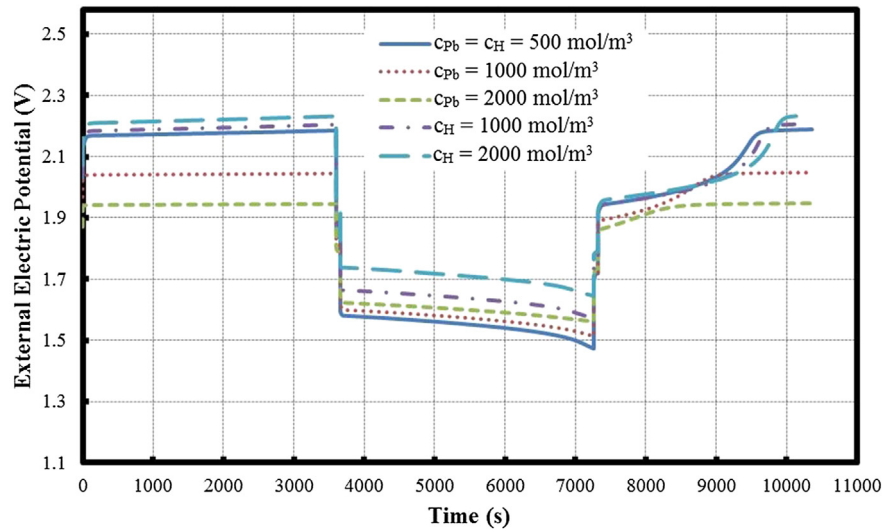


Fig. 7. External electric potential versus time for changes in initial species concentration.

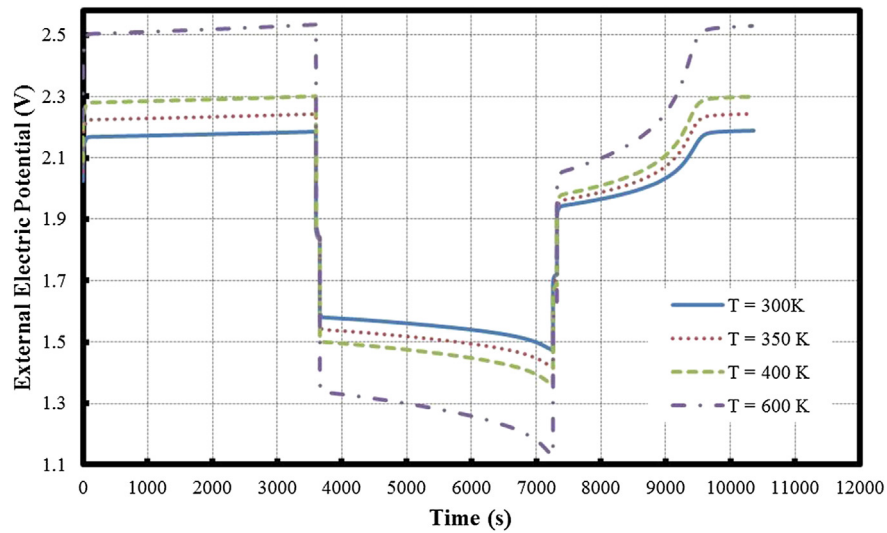


Fig. 8. External electric potential versus time for changes in cell temperature.

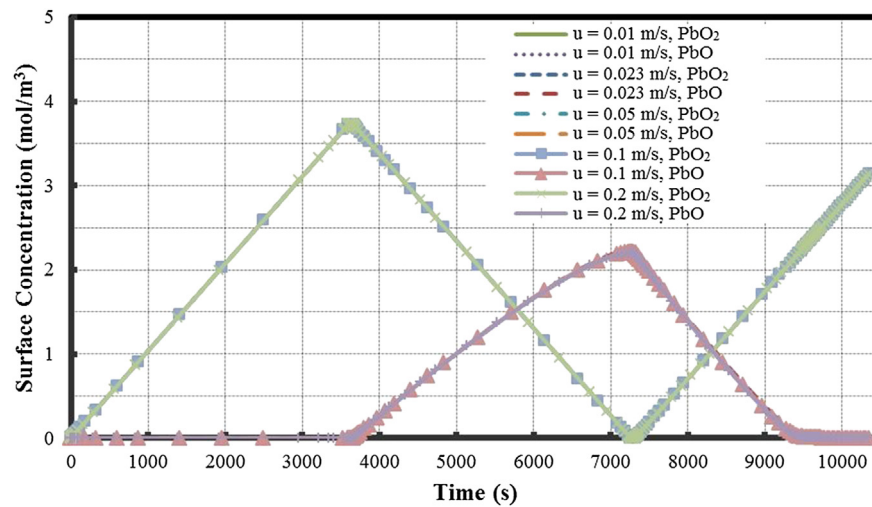


Fig. 9. Positive electrode surface concentration versus time for changes in inlet velocity.

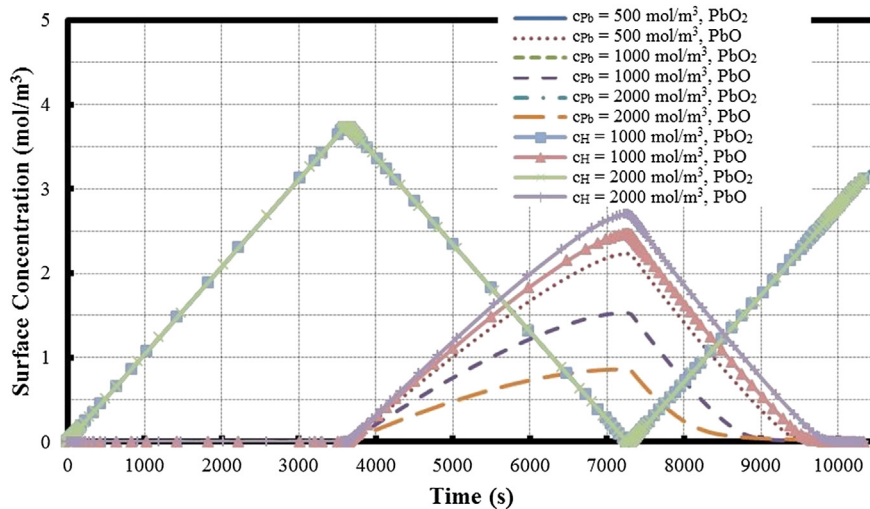


Fig. 10. Positive electrode surface concentration versus time for changes in initial species concentration.

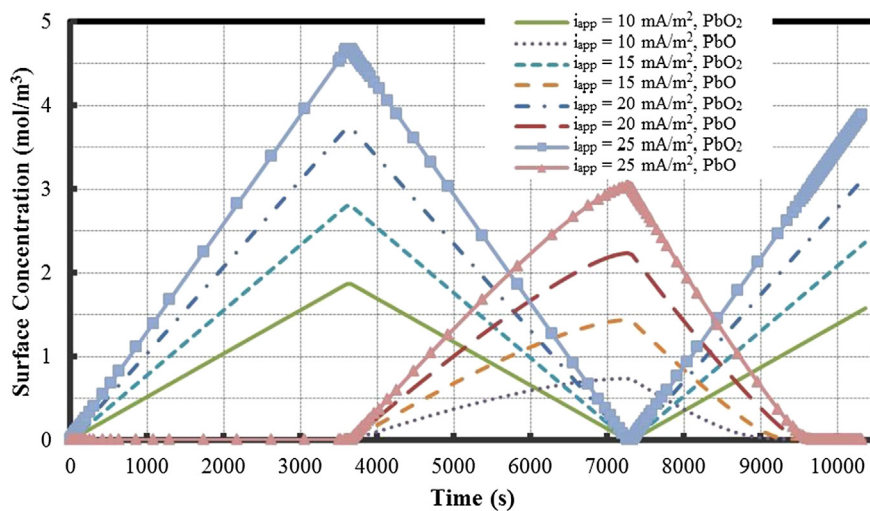


Fig. 11. Positive electrode surface concentration versus time for changes in applied current density.

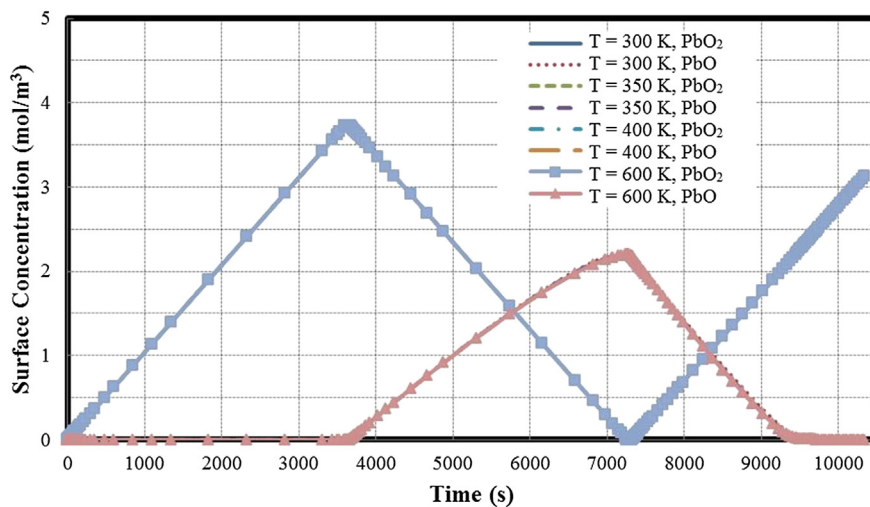


Fig. 12. Positive electrode surface concentration versus time for changes in cell temperature.

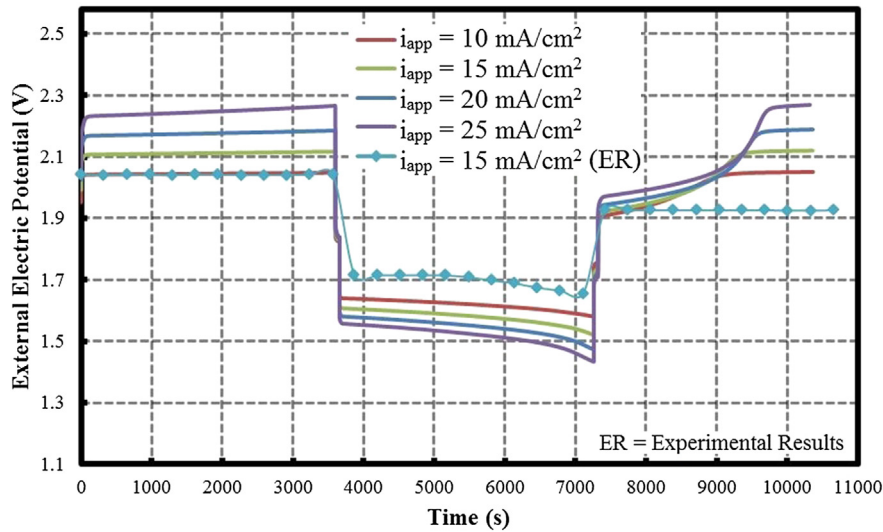


Fig. 13. External electric potential versus time for changes in applied current density with experimental data points plotted.

charge phase. Changes in temperature were applied and the effect on external electric potential versus time is shown in Fig. 8. From Fig. 8 it is seen that increases in temperature raise external cell voltage during charge; however, cell voltage is reduced significantly during discharge. Table 2 shows peak voltage values for changes in cell temperature.

The last four images, Figs. 9–12, show surface concentrations, on the positive electrode, for PbO and PbO₂ versus time for varies changes in operating conditions. Fig. 9 shows positive electrode surface concentration versus time for changes in inlet velocity. During charge the concentration of PbO₂ increases on the positive electrode and decreases during discharge. Also, PbO surface concentration increases during charge and decreases during discharge. Inlet velocity has little to no effect on positive electrode surface concentrations as seen in Fig. 9. Positive electrode surface concentration versus time for changes in initial species concentration in the electrolyte is shown in Fig. 10. The surface concentration of PbO₂ is mostly unaffected by changes in initial species concentration; but, PbO concentrations are heavily affected. Increasing initial hydrogen concentration in the electrolyte increases the surface concentration of PbO, while increasing the Pb(II) initial concentration in the electrolyte decreases the surface concentration of PbO during discharge.

The effects of changes in applied current density on positive electrode surface concentrations are shown in Fig. 11. When applied current density is high, surface concentrations of both PbO and PbO₂ increases substantially. References reported similar effects when current density was high. Likewise, low applied current density results in lower surface concentrations of both PbO and PbO₂. Peak surface concentration values of PbO and PbO₂ for changes in applied current density are shown in Table 3. The final image, Fig. 12, shows changes in positive electrode surface

concentration versus time for changes in cell temperature. Fig. 12 shows surface concentrations on the positive electrode are largely unaffected by changes in cell temperature.

Changes in external electric potential versus time for variations in applied current density are shown in Fig. 13. When the applied current density is high, external cell voltage increases during charge and decreases during discharge. With low applied current density the effect is opposite, external cell voltage is lower during charge and higher during discharge. The graph of Fig. 13 closely matches work done by Shah et al. which was experimentally validated [5]. The figure by Shah et al. begins with the second charge cycle starting at a lower external voltage and climbing close to the theoretical voltage with time. In Fig. 13 the second charge cycle is between 7200 and 10800 s. The second charge cycle in Fig. 13 begins at a lower voltage increasing toward the theoretical voltage with time. The decrease in voltage is attributed to PbO concentrations on the positive electrode surface. The peak voltages during charge and discharge, for each current density change, are shown in Table 4. Data points from experimental work were included in Fig. 13. It is seen that the experimental results closely match the results from simulation. Differences in curves were attributed to the surface area difference in electrodes. The second charge curve is

Table 2
Peak external electric potential values for change to cell temperature.

Temperature (K)	External electric potential charge (V)	External electric potential discharge (V)
300	2.15	1.54
350	2.23	1.51
400	2.27	1.47
600	2.51	1.09

Table 3
Peak surface concentration values for changes in applied current density.

Applied current density (mA cm ⁻²)	PbO surface concentration (mol m ⁻³)	PbO ₂ surface concentration (mol m ⁻³)
10	0.70	1.84
15	1.48	2.74
20	2.28	3.70
25	3.08	4.72

Table 4
Peak external electric potential values for changes to applied current density.

Applied current density (mA cm ⁻²)	External electric potential charge (V)	External electric potential discharge (V)
10	2.02	1.62
15	2.09	1.60
20	2.16	1.56
25	2.25	1.51
15 (Experimental)	2.102	1.685

believed to remain horizontal due to larger surface concentrations on the electrode as a result of the smaller surface area.

4. Conclusion

Simulations show the effects changing operating conditions have on a lead-acid flow battery. Changing the temperature of the cell has a large effect on external cell voltage and a small effect on surface concentrations. This indicates cell temperature may be a key in optimizing a lead-acid flow battery. Increasing the flow rate by 20 times reduces lead surface concentration by over 150 mol m^{-3} . Changing the flow rate this drastically may cause other issues; however, it is apparent flow rate has an impact on lead deposition. Changing the applied current density has a moderate effect on lead deposition. When the current density is increased from 10 mA cm^{-2} to 15 mA cm^{-2} the surface concentration increases by almost 50 mol m^{-3} . Varying operating conditions may be the key to controlling lead deposition which will increase the lifetime of a lead-acid flow battery.

The simulations presented in this study give valuable insight into the workings of a lead-acid flow battery. This information will

make controlling the surface deposition on the working electrodes more viable. If the electrode surface can be controlled in a routine way, the life of the cell will be extended significantly. Simulations show changing operating parameters can have a large effect on the deposition of lead. Simulations were partially validated by experimental work which closely resembled simulation results.

Acknowledgments

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